Ionic Liquids R&D-
US Air Force Research Laboratory

Molecular Dynamics Contractors Meeting

24 May 2005

Monterey CA

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **APR 2005**	2. REPORT TYPE	3. DATES COVERED **-**
4. TITLE AND SUBTITLE **Research and Development of Ionic Liquids at U.S. Air Force Research Laboratory Ionic Liquids R&D - US Air Force Research Laboratory**		5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **T Hawkins**		5d. PROJECT NUMBER **5026** 5e. TASK NUMBER **0541** 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Air Force Research Laboratory (AFMC),AFRL/PRSP,10 E. Saturn Blvd.,Edwards AFB,CA,93524-7680**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**		
13. SUPPLEMENTARY NOTES		
14. ABSTRACT **N/A**		
15. SUBJECT TERMS		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**13**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

AFRL Ionic Liquids Team

Those involved in this work

Stefan Schneider
Synthesis and Characterization

Angelo Alfano
Ignition Characterization

Gammy Vaghjiani
X-ray crystallography

Jeff Mills
Theoretical Calculations

Leslie Hall
Synthesis & x-ray work

Donald Tzeng
Synthesis and Characterization

Jerry Boatz
Theoretical Calculations

Tom Hawkins
Team Lead-Propellant Development

Why ILs as Energetic Materials?

<u>"Tuning" IL structure for</u>:
Energy content
Oxygen balance
Melting point
Liquid range

<u>Propulsion</u>:
Thrusters

<u>Explosives</u>:
Melt-cast munitions

<u>?????</u>
Power generators, APUs,….

AFRL Ionic Liquids

Why Ionic Liquids for Propulsion?

- A figure of merit (FOM) can be based on the momentum imparted by a HEDM normalized by that of a standard material (e.g., NTO/MMH)
- Two main properties
  1) Average kinetic energy (KE) of gases produced per unit mass of HEDM combusted/decomposed
  2) Density (ρ) of material

$$FOM = [(2KE_{HEDM})^{1/2} \ln(1 + c'\rho_{HEDM})] / [(2KE_{STAND})^{1/2} \ln(1 + c'\rho_{STAND})]$$

(where, c' = Material volume/Mass of combustor; and set to 1.0 m^3/kg)

KE ↑

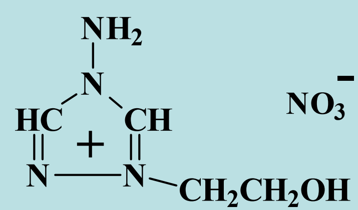
Tc ↑

ΔHf ↑

	NTO-HEHN	NTO-HEATN	NTO-MMH
KE (MJ/kg)	3.9	4.0	4.7
ρ (kg/m^3)	1424	1454	1189
FOM (STAND=NTO/MMH)	1.03	1.05	1.0

$[HOCH_2CH_2N_2H_4]^+ \; NO_3^-$

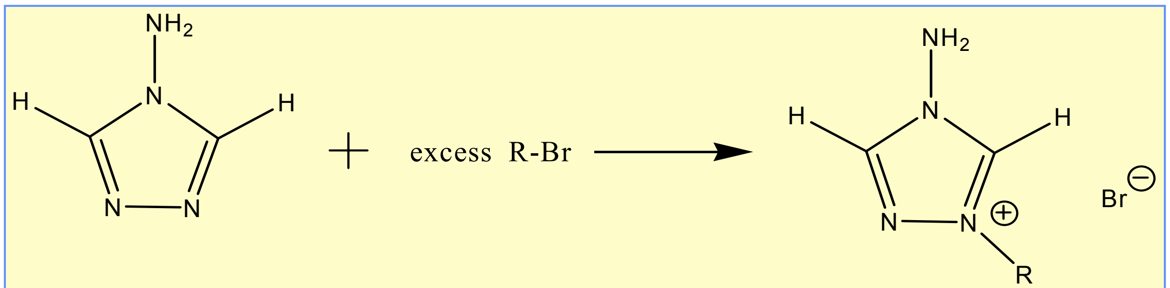
HEHN; ρ= 1.42 g/cc; MP <-25C



HEATN; ρ= 1.48 g/cc; MP = 0C

Recent Ionic Liquid Synthesis and Characterization

- Energetic ILs synthesized based on heterocyclic cations
  - Extending foundation of IL work pioneered at AFRL*
  - Recent work in production of higher energy analogues of 1-hydroxyethyl-4-amino-1,2,4-triazolium nitrate
    - Replacement of the hydroxyl with energetic substituents (-CN,-N_3…)
      - Nitrile increases energy content (e.g., ethanol: ΔH_f= -1220 cal/g; acetonitrile: ΔHf= +300 cal/g)



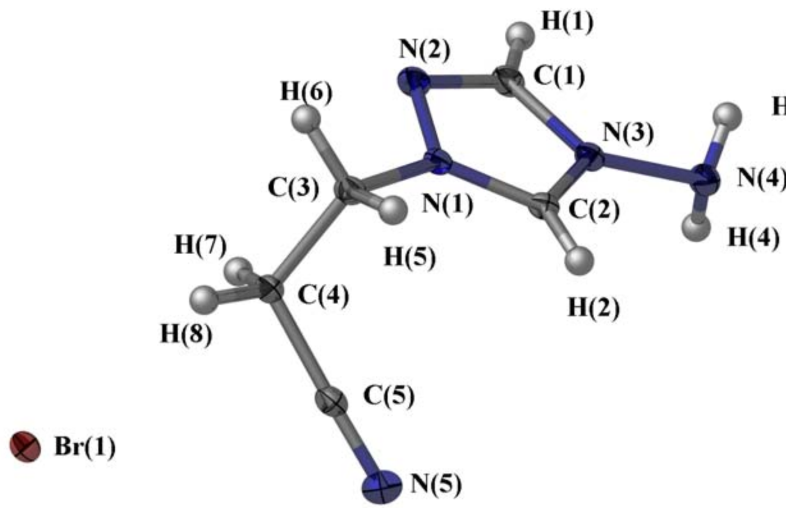
First step of two-step process

Where R = acetonitrile and propionitrile

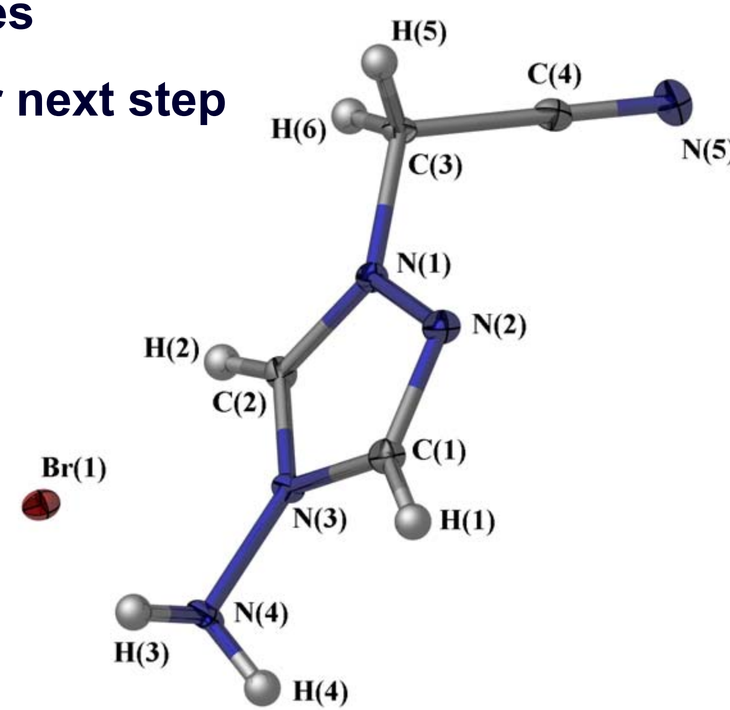
"1-R-4-Amino-1,2,4-triazolium Salts: New Families of Ionic Liquids" , G. Drake, T. Hawkins, K. Tollison, L. Hall, A. Vij and S. Sobaski in ACS Symposium Series 902 (Oxford University Press): Ionic Liquids IV: Fundamentals, Progress, Challenges, and Opportunities (2005)

Recent Ionic Liquid Synthesis and Characterization

- First step successfully performed
  - Crystal structures obtained for bromides
  - Oxygen-bearing anions substitution for next step

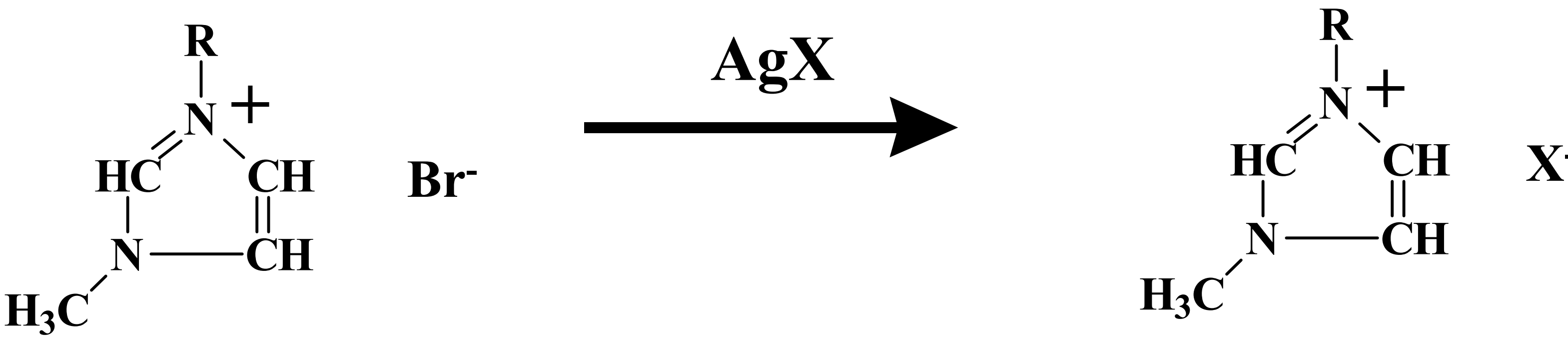


1-cyanoethyl-4-amino-1,2,4-triazolium bromide



1-cyanomethyl-4-amino-1,2,4-triazolium bromide

AFRL Ionic Liquids



1-propargyl-3-methyl-imidazolium bromide

$X^- = C_2N_3^-, NO_3^-, ..$

COMPOUND	STRUCTURE	$\Delta H_f/C$ Kcal/mol
Ethane	CH_3CH_3	-5
Ethylene	$CH_2=CH_2$	+6.25
Acetylene	CH=CH	+27.1

SALT	Melting Point	Decomposition Onset
1-propyl-3-methyl-imidazolium bromide*	~ -14 ° C	-
1-allyl-3-methyl-imidazolium bromide	62 ° C	~ 220 ° C
1-propargyl-3-methyl-imidazolium bromide	112 ° C	180 ° C
1-propargyl-3-methyl-imidazolium dicyanamide	15 ° C	143 ° C
1-propargyl-3-methyl-imidazolium nitrate	in progress	in progress

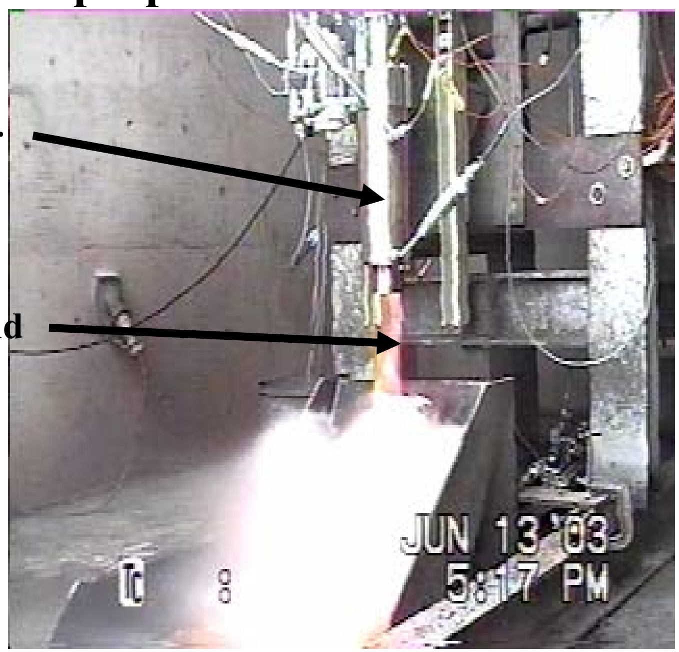
* J.D. Holbrey & R.D. Rogers, “Melting Points and Phase Diagrams”, Ionic Liquids in Synthesis, P. Wasserscheid and T. Welton (Eds.), Wiley-VCH (2003).

Ionic Liquid Fuel for Bipropulsion

Goal: Demonstrate feasibility of ionic liquid as fuel for bipropellant systems

Accomplishment

- AFRL/PRSP working with Purdue University has successfully tested high performance ionic liquid fuel in a bipropellant thruster

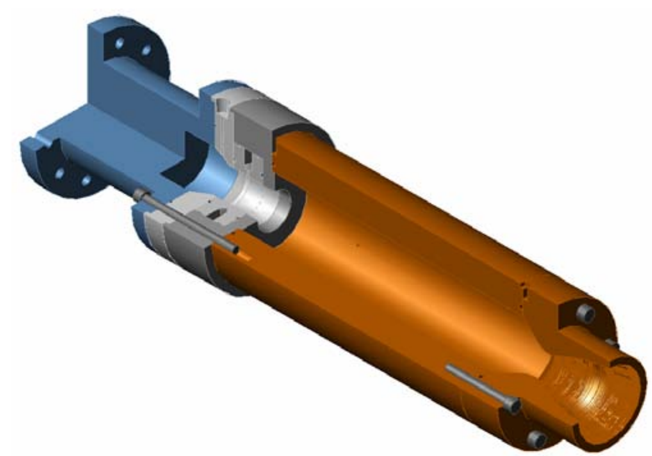


Thruster during bipropellant operation (93% C* efficiency)

Significance

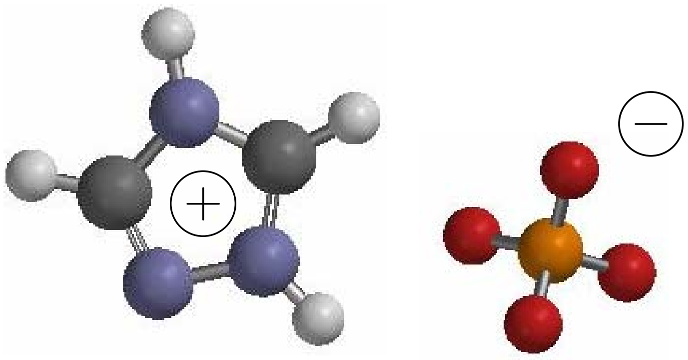
- Storable bipropellant system with potential increase in performance over NTO/MMH
- Greatly reduced toxicity vs NTO/MMH

Staged bipropellant thruster for ionic liquid fuel

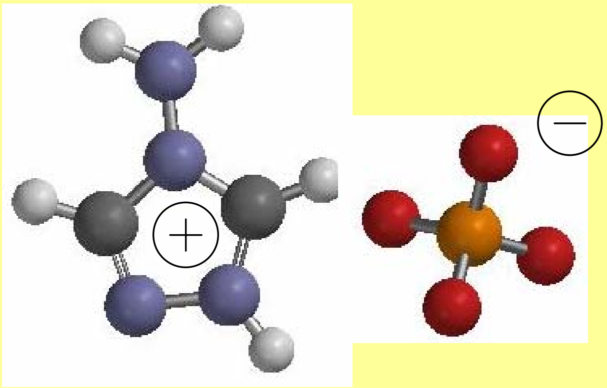


Ionic Liquids in Munitions

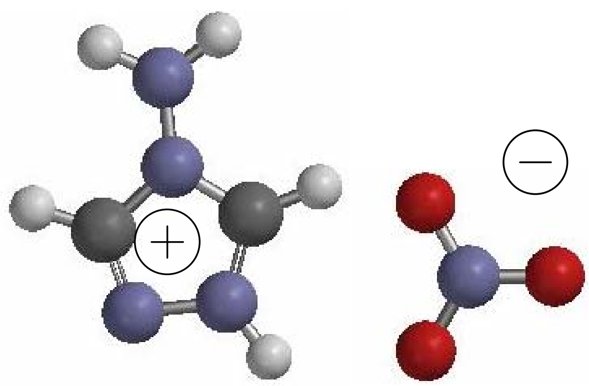
- Triazolium salts initially synthesized at USAF
- Scaled to the 50 gram level and characterized in ONR program



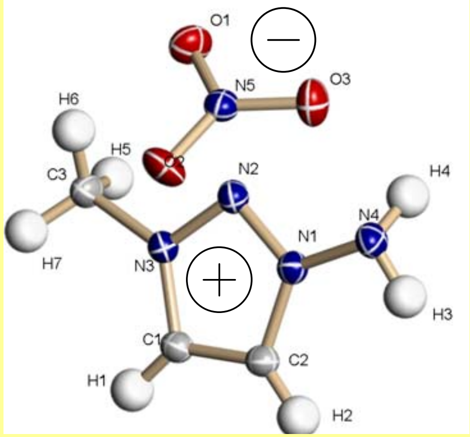
1,2,4-triazolium perchlorate



4-amino-1,2,4-triazolium perchlorate (4-ATP)



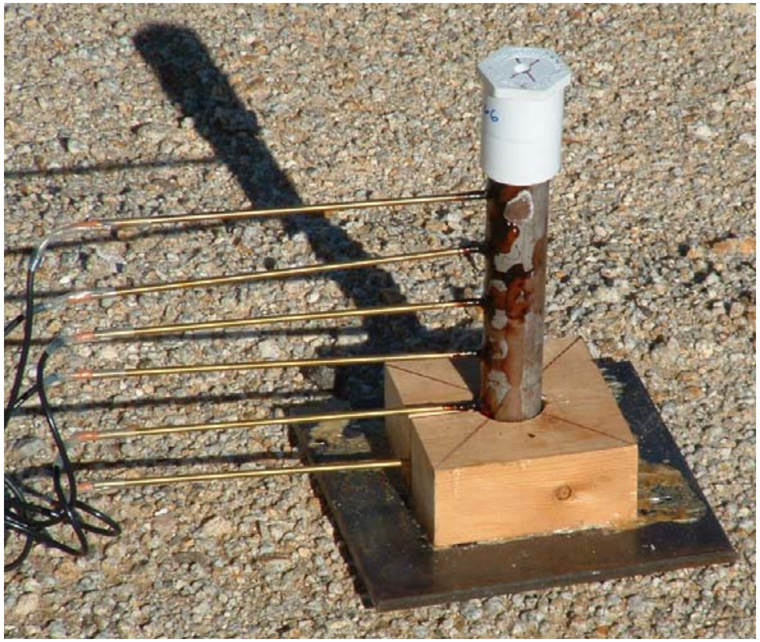
4-amino-1,2,4-triazolium nitrate



1-amino-3-methyl-1,2,3-triazolium nitrate

Energetic Ionic Liquids for TNT replacements

Very promising initial results!!



Shock velocity determination

- **4-ATP (melt cast) ρ = 1.74 g/cm^3; shock velocity = 8.3 mm/usec**
- **TNT (pressed) ρ = 1.63 g/cm^3; shock velocity = 6.9 mm/usec (LLNL Data)**

4-ATP is approaching energy output of high melt point, state-of-the-art nitramines like RDX !

Theoretical Performance

Calculations indicate that triazolium salts and mixtures are <u>capable of achieving/exceeding performance goals</u>

Ingredients (Composition, Wt/Wt)	Total Detonation Energy (KJ/cc)	Shock Velocity (mm/μs)	C-J Pressure (GPa)
TNT	7.716	6.886	19.57
4-ATP	9.032	8.368	29.94
AMTN	7.923	8.115	23.58

- Research program funded for FY05
  - Continues production of IL-based molecules for munitions
  - Scale-up of triazole-based ionic liquid in progress for additional characterization

AFRL Ionic Liquids

Summary and Conclusions

- Both straight chains and heterocycles offer scaffolds for energetic ILs
  - N-amino heterocycles offer a rich platform for ionic liquids
  - Synthesis of novel, heterocycle-based ILs is occuring through introduction of energetic functionalities
  - X-ray crystallography continues to be a powerful tool in our arsenal of characterization tools- confirming structure and identifying interactions in the solid state
  - Understanding ignition and combustion of IL molecules will be a key to future uses
- ILs offer promising avenues for HEDM transition to applications

AFRL Ionic Liquids

Acknowledgements

Collaborators

Greg Drake (NASA-Marshall)
Adam Brand (AFRL/PRSP)
Milton McKay (AFRL/PRSP)
Jo ann Larue (AFRL/PRSP)
Suresh Suri (AFRL/PRSP)
Scott Shackelford (AFRL/PRSP)
B.J. Austin (IN-Space/Purdue)
Steve Heister (Purdue)
Jeff Bottaro (SRI)
Mark Petrie (SRI)
John Wilkes (USAFA)

Sponsors

Mike Berman (AFOSR)
Mike Huggins (AFRL/PRSP)
Judah Goldwasser (ONR)
Cliff Bedford (ONR)
Ronald Channell (AFRL/PRSP)
Wayne Kalliomaa (AFRL/PRSP)
Robert Corley (AFRL/PRS)